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ABSTRACT

The essence of this AFOSR project is to investigate the structure, composition, mode of attachment and reactivity of the molecular species which form at the surfaces of metals in contact with fluids. Progress to date includes advances in investigative technology, 110 scientific articles, and useful findings as follows: A series of new findings, advances in investigative technology and 105 scientific articles have occurred thus far. These include (i) determination of molecular orientations and modes of attachment at electrode surfaces; (ii) demonstration that mode of surface attachment affects electrochemical reactivity; (iii) exploration of the structure and composition of electrodeposited metal monolayers and thin-films; (iv) investigation of the nature of the species formed at electrode surfaces in ionic solutions; (v) adaptation of high-resolution electron energy-loss spectroscopy (HREELS) to measurement of vibrational spectra of species adsorbed at electrode surfaces; (vi) systematic HREELS, Auger and electrochemical studies of families of adsorbates, including acids, alcohols, alkenes, amines, mercaptans, phenols and pyridines; (vii) demonstration of the stability of chemisorbates in vacuum; (viii) development of techniques for measurement of complete Auger emission angular distributions potentially useful for structure probing of solid surfaces; (ix) development of an infrared (IR) reflectance spectrometer capable of recording the vibrational spectra of typical adsorbed organic molecules; and (x) studies of the interaction of the polar solvent acetonitrile with solid electrode surfaces.

I. REPORT OF RESEARCH

Briefly, this AFOSR-funded research project has explored molecular orientation, bonding, and reactivity at electrode surfaces, investigated the structures of electrodeposited metallic monolayers, observed the electrochemical reactivity of adsorbed molecular species, characterized surface layers formed by adsorption of ions, and examined adsorbed molecular species at electrode surfaces by means of AES, HREELS, LEED, and related techniques*. The results of these investigations are described in 110 publications (listed in Section II).

A. Motivations for Research in Surface Electrochemistry

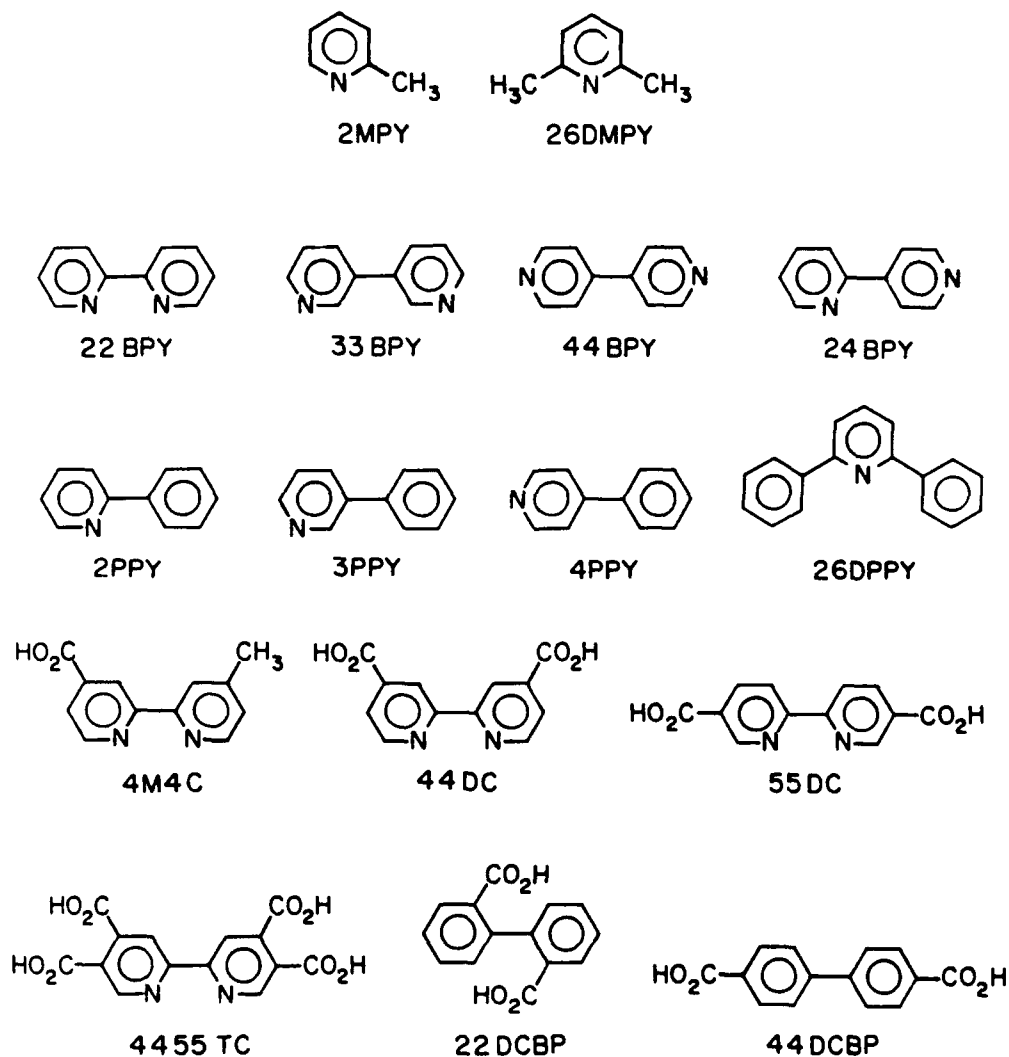
Before reporting the results of our research on the electrochemistry and spectroscopy of metal surfaces (June 1, 1990 - April 30, 1993), let us reflect on the basic reasons for making studies of this type. There is a need for direct methods by which to detect, identify, and quantitate the surface atomic, ionic and molecular layer which controls the practical behavior of metals in vital situations such as bonding of metals, protection of metal surface finish, lubrication of metal surfaces, electrochemical energy storage, cleaning of metallic materials, and fabrication of metallic/semiconductor thin-film electronic devices and sensors. There is also a need for knowledge regarding the chemical reactions which occur between important classes of chemical substances and various material surfaces. Such information is vital to design of material handling processes and devices, batteries, electronic microcircuits, composite materials, device fabrication procedures, high performance lubricants, protective coatings and other surface-related practical development projects. Accordingly, we are developing methods, instrumentation, and software for probing of electrode surface structure by means of LEED and Auger spectroscopy, investigating surface molecular structure and bonding by use of HREELS and IR spectroscopy, and exploring surface electrochemical reactivity by means of cyclic voltammetry and chronoamperometry. With these methods we can now detect, identify, and quantitate any substance on any surface in any practical amount. Our latest findings are summarized below and in the publications listed in Section II.

* AES = Auger Electron Spectroscopy
HREELS = High Resolution Electron Energy-Loss Spectroscopy
LEED = Low-Energy Electron Diffraction

B. Molecular Electrochemistry at Metal Surfaces

Several important families of organic compounds have been explored with respect to their chemical and electrochemical reactivity towards Pt and Ag single-crystal surfaces (publications 133, 139, 141, 142-144, 146, 147, 151, 158, and 182, listed in Section II). Powerful new methodology was developed in order to make such determinations possible for the first time. Compounds were chosen with regard to their appropriateness for exploring various important surface chemical and electrochemical processes. Methods, rationale, results and implications are summarized below and in the publications.

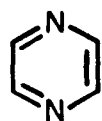
Bipyridyls, methyl-pyridines and bipyridyl carboxylic acids were studied (133) in view of earlier results for pyridine carboxylic acids (125) to explore the influence of steric hindrance at the ring nitrogens, which are predominantly responsible for the chemisorption of such compounds at Pt electrodes (125, 133):



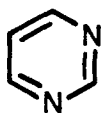
These are 2,2'-bipyridyl (22BPY); 2,4-bipyridyl (24BPY); 3,3'-bipyridyl (33BPY); 4,4'-bipyridyl (44BPY); 2-phenylpyridine (2PPY); 3-phenylpyridine (3PPY); 4-phenylpyridine (4PPY); 2,6-diphenylpyridine (26DPPY); 2-methylpyridine (2MPY); and 2,6-dimethyl-pyridine (26DMPY). Carboxylic acid derivatives (supplied by Professor C. Michael Elliott, Colorado State University) were studied to explore the interactions between carboxylate moieties and the Pt(111) surface: 2,2'-biphenyldicarboxylic acid (22BPDC); 4,4'-diphenyl-dicarboxylic acid (44BPDC); 2,2'-bipyridyl-4,4'-dicarboxylic acid (44DC); 2,2'-bipyridyl-4-methyl-4'-carboxylic acid (4M4C); 2,2'-bipyridyl-5,5'-dicarboxylic acid (55DC); and 2,2'-bipyridyl-4,4',5,5'-tetracarboxylic acid (4455TC). Packing densities (moles adsorbed per unit area) were measured by means of AES. Electrochemical reactivity of the chemisorbed layer was explored by means of CV. Vibrational modes of the surface layer were observed by means of HREELS. Long-range order of the Pt(111) substrate surface and adsorbed layer was checked by means of LEED. Compounds having an unhindered pyridyl ring nitrogen are chemisorbed with the ring system nearly perpendicular to the surface (2MPY; 33BPY; 44BPY; 2,4-DPY; 3PPY; 4PPY). However, chemisorption with the rings parallel to the surface occurred for compounds having only hindered ring nitrogen atoms (26DMPY; 26DPPY) or no aromatic nitrogens at all (22BPDC; 44BPDC). Chemisorption with one ring perpendicular and the other parallel occurred with the compounds having one hindered and one unhindered ring-nitrogen (2PPY; 22BPY; 4M4C; 44DC; 55DC; 4455TC). Vibrational frequencies observed by HREELS correspond to frequencies observed by FTIR for the unadsorbed compounds, such that assignment of the HREELS spectra can be made rather easily with reference to standard spectra. All of the adsorbed bipyridyl carboxylic acids react to at least some extent with KOH. In contrast, the adsorbed biphenyl carboxylic acids are relatively inert. Chemisorption of the bipyridyl carboxylic acids at relatively positive electrode potentials (0.4V vs. Ag/AgCl) results in chemical interaction between the carboxylate groups and the Pt surface, as evidenced by lower intensities and frequencies of vibrations due to O-H and C=O stretching, and aromatic CC modes. As expected, the biphenylcarboxylic acids are evidence of chemisorption with the rings parallel to the surface and strong interaction between the carboxylate moieties and the Pt surface at all electrode potentials studied. Chemisorption of an aromatic ring parallel to the Pt surface strongly activates the electrochemical oxidation process, relative to the perpendicular orientation which is relatively inert.

Multinitrogen heteroaromatics adsorbates and some carboxylic acid derivatives have been studied at Pt(111) surfaces in contact with aqueous electrolytic solutions (139) in order to explore the surface interactions of multiple aromatic ring nitrogens: pyrazine (PZ); pyrimidine (PM); pyridazine (PZ); triazine

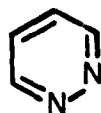
(TZ); 2-pyrazine carboxylic acid (PZCA); 2,3-pyrazinedicarboxylic acid (23PZCA); and 4-pyridazinecarboxylic acid (4PDCA):



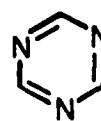
PZ



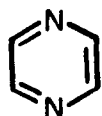
PM



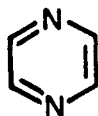
PD



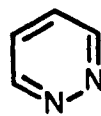
TZ



PZCA



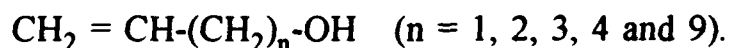
23 PZDCA



4 PDCA

Each chemisorbs at Pt(111), with the notable exception of TZ. Data from AES, HREELS, LEED and CV indicate that these adsorbates are oriented with the ring approximately perpendicular to the Pt surface ($75\text{--}85^\circ$ ring-to-surface angles). The adsorbed layer is lacking in long-range order, although the Pt surface remains ordered during aromatic adsorption. Only one of the ring-nitrogens chemisorbs to the surface in each instance. Interaction of the carboxylate moieties with the surface is potential-dependent.

Terminal alkenols have been studied (141) with respect to chemisorbed state and electrochemical reactivity at a Pt(111) electrode in aqueous solution as a function of aliphatic chain length:



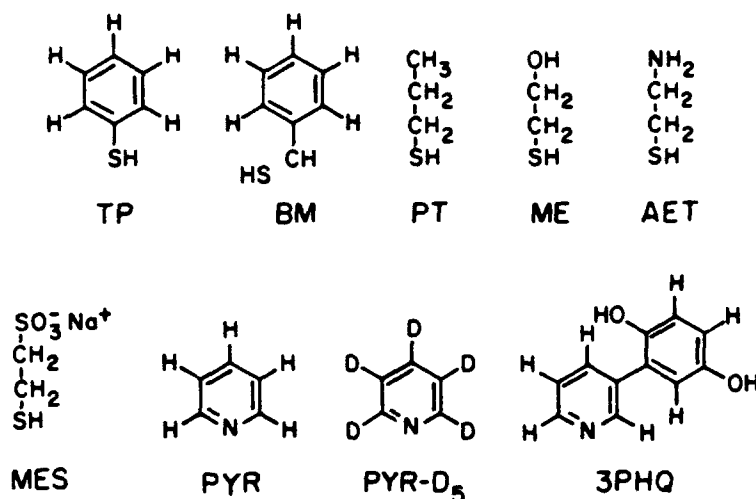
Chemisorption of these compounds to Pt is primarily through the C=C double-bond (HREELS) rather than the OH moiety. Regardless of chain-length ($n = 1$ to 9) each alkenol molecule occupies an area similar to that of the smallest compound in the series, 2-propene-1-ol (PPEOH, "allyl alcohol"), indicating that the aliphatic chain and OH moiety are pendant. The OH is in contact with the Pt surface only for PPEOH. An O-H stretching (3354 cm^{-1}) band was detected by HREELS only for adsorbed 3-butene-1-ol (BTEOH). Evidently, the OH stretching band is strongly perturbed by intermolecular hydrogen-bonding for PTEOH ($n = 3$), HXEOH ($n = 4$), and UDEOH ($n = 9$), and by interaction of OH with the Pt surface for PPEOH. Measurements by AES and chronocoulometry of the average numbers of electrons

transferred (n_{ox}) in electrochemical oxidation of each adsorbed alkenol molecule indicates that oxidation takes place almost exclusively at the C=C double-bond and the one adjacent C atom (that is, at the three C atoms closest to the Pt surface).

Terminal alkenes, $CH_2 = CHC_nH_{2n+1}$ (where $n = 0, 1, 2, 3, 4, 6$, and 8) have been studied likewise (142). The corresponding alkanes are not chemisorbed from aqueous solutions onto Pt(111), at least under the conditions of these experiments (40). Molecular packing densities measured by means of AES suggest that in the average molecular orientation of chemisorbed terminal alkenes the C=C moiety is parallel to the Pt surface and the alkyl chain is pendant, although further research on this point would be advisable. HREELS spectra indicate that the C=C bond is preserved in some or all of the adsorbed material for each of the alkenes studied. As for the alkenols, electrochemical oxidation of the adsorbed alkene layer in aqueous electrolyte involves primarily the C=C moiety and one adjacent carbon atom.

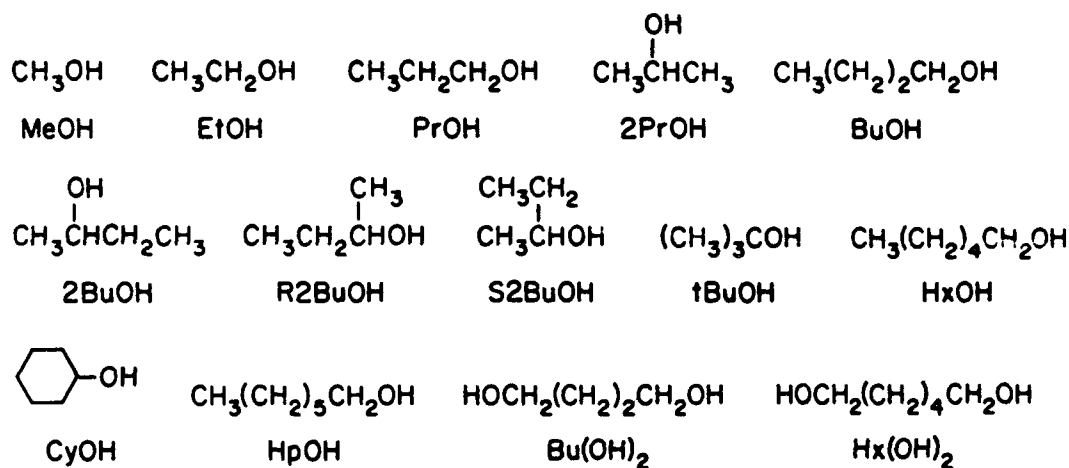
Chemisorption of 2-pyridinethiol (2PyT) and 4-pyridinethiol (4PyT) at Ag(111) electrode surfaces has been studied as a function of electrode potential (147). A motivation for this study was to observe the vibrational spectra of pendant pyridyl rings indirectly attached to an electrode surface. Attachment of 2PyT and 4PyT to the Ag(111) surface at electrode potentials less than about -0.2V (vs. Ag/AgCl) occurs predominantly by dissolution of the sulfhydryl hydrogen and formation of a S-Ag bond. HREELS spectra following adsorption below about -0.4V closely resemble the IR spectra observed for unadsorbed 2PyT and 4PyT. However, at potentials more positive than 0.0V, a coupling reaction occurs between adsorbed and dissolved mercaptopyridines to form a bimolecular layer; this coupling reaction is most noticeable for 4PyT. The adsorbed layers exhibit long-range order readily detected by means of LEED. Layer structure is potential-dependent (details are given in ref. 147). The pyridyl ring is perpendicular to the Ag(111) surface and the packing density is essentially constant at all concentrations studied (10^{-5} M to 0.2 M).

Related studies of mercaptans have explored the adsorption behavior of this important family of adsorbates at Pt(111) and Ag(111) for a representative series of molecular classes and structures: thiophenol (TP); benzylmercaptan (BM); 1-propanethiol (PT); 2-mercaptoethanol (ME); 2-aminoethane thiol (AET); 2-mercaptoethane sulfonic acid sodium salt (MES); pyridine (PYR); pyridine- d_5 (PYR- d_5); and (3-pyridyl)-hydroquinone:



AES and HREELS data indicate that all of these mercaptans are attached to Pt(111) and Ag(111) surfaces primarily through the S-atom with dissociation of the sulfhydryl hydrogens, the remainder of the molecule being pendant. Packing densities (AES) are in close agreement with theoretical limiting packing densities based upon molecular models. HREELS spectra of the adsorbates display the same vibrational frequencies as the IR spectra of the unadsorbed compounds, indicating retention of molecular framework in the adsorbed state. The pyridines (PYR; PYR-d₅; 3PHQ) chemisorb at Pt(111) but not at Ag(111). These mercaptans exhibit noticeably greater long-range order at Ag(111) than at Pt(111).

Saturated alcohols have been studied at Pt(111) electrodes with respect to the nature and electrochemical reactivity of the adsorbed species (158):



Represented by this selection of alcohols are: a range of alkyl chain lengths (MeOH, EtOH, PrOH, BuOH, HxOH, HpOH); branching adjacent to OH (2PrOH, 2BuOH, t-BuOH); chirality adjacent to OH (R2BuOH, S2BuOH); influence of an alkyl chain adjacent to OH (CyOH); and the presence of two OH moieties [Bu(OH)₂, Hx(OH)₂]. Each of these alcohols chemisorbs at Pt(111) from aqueous fluoride electrolytes. Conditions of these experiments were: pH = 4 (KF/HF); electrode potential, -0.1V vs. Ag/AgCl; alcohol concentration, 0.1M or saturation, whichever is smaller. Surface attachment of these saturated alcohols is through the oxygen atom, with probable involvement of the adjoining carbon atom. The aliphatic chains or rings are in contact with the Pt surface for most of these alcohols; the exceptions are Hx(OH)₂, for which the alkyl chain and one OH is pendant, and t-BuOH, which has a pendant t-Bu moiety. Short-chain alcohols such as MeOH, EtOH, PrOH, 2PrOH, BuOH and Bu(OH)₂ undergo partial decomposition to form an adsorbed layer consisting primarily of CO and an alkoxide. Electrochemical oxidation of these chemisorbed saturated alcohols takes place primarily at the carbon atom adjacent to the surface-attached alcohol oxygen atom(s).

Methane electro-oxidation at Ru(001) electrodes in aqueous electrolytes has been studied (182) in order to seek the causes for reported potent catalysis of methane oxidation by Ru electrodes. Various surface pretreatment procedures were investigated with emphasis on the resulting state of the Ru surface and the rate of oxidation of methane. Immersion of Ru(001) into pure water at open circuit forms a layer of adsorbed hydrous oxides having an ordered (2 x 2) structure (LEED, HREELS). Anodization of Ru(001) in 1M HClO₄ produces an ordered (1 x 1) film of RuO/OH consisting of several atomic layers (AES, HREELS, LEED), which is not removed by electrolysis at negative potentials near the onset of hydrogen evolution. Electrodeposition of Ag in submonolayer, monolayer and multilayer amounts with or without the O/OH overlayer produces a continuous Ag film lacking in long-range order. Under the present conditions, namely surfaces of Ru(001) with or without O/OH and/or Ag overlayers in aqueous electrolytes, the faradaic current due to oxidation of methane is generally rather small (less than 1 μ A/cm²). Evidently, the potent catalysis reported by various workers results primarily from specific details of the surface preparation, oxidation rate measurements, and calculations which have not yet been repeated under well-defined conditions; more research will be required.

C. Auger Emission Angular Distributions

Auger electron emission angular distributions have been measured with relatively high precision over virtually the complete range of angles of emission for

a variety of well-characterized electrode surfaces (135, 148, 154, 159, 161, 164, 166, 167, 170). The long-term motivation for this work is to perfect a method by which to probe the structures of electrode surfaces and of adsorbed atomic, ionic, and molecular layers to a depth of several atomic layers. Steps along the way to this goal are: to measure the Auger angular distributions with sufficient precision, accuracy, angle range, angle resolution and energy resolution that the features of the distributions can be clearly visualized and quantified (this step includes development of innovative instrumentation and software); to measure distributions for a series of "reference" surfaces which have been characterized by means of LEED, STM, X-ray crystallography and HREELS; to develop innovative software by which to display, analyze and evaluate the data; to compare the computer-generated predictions of various published theories with the experimental data for well-defined surfaces; and, guided by experiment, to evolve a practical quantum mechanical theory for use in deducing surface structures from measured distributions.

We have measured complete Auger emission angular distributions for a variety of samples:

- Ag(111) at kinetic energy, KE = 15, 20, 25, 30, 35, 40, 45, 49, 55, 60, 65, 81, 153, 358, and 2000 eV (156, 166);
- Pt(111) at KE = 65, 161, 252, and 1968 eV (152);
- W(100) at KE = 52, 178, 350, and 1760 eV (178);
- Pt(111)($\sqrt{3} \times \sqrt{3}$)R30°-I, Pt(111)($\sqrt{7} \times \sqrt{7}$)R19.1°-I and Pt(111)(3 x 3)-I at KE = 65, 161, 252, and 1968 eV (Pt) and KE = 518 eV (iodine) (167, 170, 179);
- Al(100) at KE = 64 and 1388 eV (Al) (175), and at intervals of about 50 eV from KE = 10 to 1500 eV (188);
- Metal dichalcogenides, such as 1T-TaS₂ (180);
- Bi₂Sr₂CaCu₂O₈ single-crystal high T_C material at KE = 289 eV (Ca), 516 eV (oxygen), and 920 eV (Cu) (189);
- SiC epitaxial thin-films grown on Si(100) at KE = 268 eV (C), and 86 and 1605 eV (Si) (185);
- Ag thin films consisting of 1, 2, 3, ..., 10, 20, 50 and 100 monolayers electrodeposited epitaxially onto Pt(111) (157).

Results for monoatomic layers of independently determined structure indicate that signal minima are observed along the principal interatomic directions even at KE greater than 500 eV. Distributions from single-crystal surfaces display minima along interatomic directions at KE less than 100 eV, and maxima along the

directions of open channels (which are also the interatomic directions). Elastic scattering angular distributions always contain features attributable to electron channeling; the locations of these features are the same as those in Auger distributions at comparable energies. Angular distributions from single-crystal substrates contain no new features when measured in the presence of an ordered adsorbed atomic layer; attenuation of substrate intensity by the monolayer is essentially isotropic, evidently due to averaging of the angular variations over the myriad emitter-scatterer geometric relationships for such samples. Distributions from ordered atomic bilayers reveal that the Auger signal from the underlayer is attenuated anisotropically and is not increased along any direction of emission. Sharply delineated Auger distributions are obtained from all of the wide variety of ordered surfaces studied thus far.

After our initial results of this type were published, several workers expressed surprise at the results, which they perceived to be in conflict with quantum mechanics and therefore incorrect (160, 162). However, subsequent work in our laboratories and elsewhere has confirmed the correctness of our experimental findings (171, 175).

The remaining controversy now seems to revolve around whether the experimental trends which we have unveiled can be explained and represented by use of existing models and algorithms, or whether a new theoretical approach is required. Several workers are now attempting to develop theoretical models to explain our results. Guided by a growing body of experimental data, we too are developing a theoretical model and computational code which include both elastic scattering and inhomogeneous inelastic scattering. We seek strict quantitative agreement between the theoretical model and the experimental distributions for samples the structure of which are known independently from LEED, STM and X-ray diffraction. Among the challenges: description of the nature of the source wave; representation of the differential and radial cross-sections of electron scattering versus Auger electron KE; rigorous description of the elastic and inelastic scattering processes; and description of channeling and other multiple-scattering effects.

D. Well-Defined Infrared Detector Surfaces

Preparation of well-ordered mercury cadmium telluride (MCT) infrared-sensitive surfaces has been demonstrated for the first time (168). MCT is an important material, widely used by the US Air Force as the photoconductive pn-junction heart of the infrared (IR) detector devices employed for infrared cameras, telescopes, weapons guidance systems, and night-vision equipment. Preparation of well-ordered MCT surfaces is important because it provides the high-quality thin-

film junctions needed for fabrication of the next generation of more sensitive and reproducible IR detectors and arrays. Our collaborator, a leading manufacturer of IR sensors [Santa Barbara Research Center (SBRC) division of Hughes Aircraft Company] reports ten-fold improvements in performance and thirty-fold increases in the yield of useful devices as a result of improvements in thin-film preparation.

In these studies a single-crystal of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$, grown at SBRC, was oriented by X-ray reflection and annealed and polished such that the parallel main-faces of a disk are metal-terminated (111-A) and Te-terminated (111-B) surfaces. These surfaces were characterized by AES, HREELS, LEED and CV at each stage of etching with methanolic bromine solution and Ar^+ ion-bombardment. After polishing, both surfaces were found to be contaminated with C and S-containing impurities and deficient in Cd; the surface was disordered. This stage was the usual starting point for fabrication of commercial IR devices. Etching decreased the S-content but did not improve surface ordering. Ion-bombardment removed C and S, restored Cd to expected levels, but left the surface disordered and deficient in Hg. A special appendage was constructed by which the MCT sample could be annealed in Hg vapor and Ar at controlled partial pressure of Hg against an ultra-high vacuum background. After annealing, the (111-A) and (111-B) surfaces displayed well-ordered structures (LEED) having the expected stoichiometry (AES) and vibrational bands (HREELS). The (111-B) face tends to facet during annealing, while the (111-A) face forms a simple (2×2) surface lattice analogous to the (111) face of diamond. These surfaces are stable in vacuum and in Ar. Use of the well-ordered (111-A) surface for device fabrication yields excellent results, as might now be expected in terms of first principles.

The next steps in this happy progression involve preparation of MCT ordered epi-layers, and capture of the epi-layer with a well-defined insulating overlayer. Work is continuing.

E. Ruthenium Electrodes for Hydrocarbon Fuel Cells

Potent catalysis by Ru electrodes has been reported by various workers. Reported here (182) are studies of chemisorption, surface vibrational spectroscopy and electrochemical reactivity at Ru(001) single-crystal electrode surfaces. Electrochemical oxidation of methane on these Ru electrode surfaces in aqueous electrolytes was investigated. Influences of surface oxide and electrodeposited silver on methane oxidation were explored. Immersion of Ru(001) into pure water at open circuit forms a layer of adsorbed hydrous oxides having an ordered (2×2) structure as measured by Auger spectroscopy and LEED. Anodization of Ru(001) in 1M HClO_4 produces a disordered Ru O/OH film consisting of several atomic layers. The HREELS spectrum of this O/OH layer exhibits Ru-O and O-H

stretching bands, and the layer is not removed by subsequent electrolysis at negative potentials. Various submonolayer and multiple-layer amounts of silver were electrodeposited on Ru(001). A continuous film is formed, based upon attenuation of the substrate Auger signal. The silver layer lacks long-range order, as judged by LEED. Under the present conditions, namely Ru(001) single-crystal surfaces with or without the O/OH and/or silver layers in aqueous electrolytes, the faradaic current due to oxidation of methane is generally less than $1 \mu\text{A}/\text{cm}^2$.

F. Non-Aqueous Solvents at Electrode Surfaces

Electrochemical studies at a carefully characterized Pt(III) electrode surface are yielding useful insights into atomic, ionic and molecular electrochemistry at interfaces. Reported here are studies of the chemisorption of the common polar aprotic solvent acetonitrile (CH_3CN) at a Pt(III) surface (194). Electrosorption of CH_3CN under typical electrolytic conditions from CH_3CN electrolytes, CH_3CN aqueous electrolytic solutions and CH_3CN vapor was investigated by HREELS, AES, LEED, and linear potential scan cyclic voltammetry (CV). The results indicate that a chemisorbed layer is formed from CH_3CN liquid, vapor, and typical aqueous solutions. The chemisorbed layer: consists of a mixture of species related to CH_3CN and acetamide (CH_3CONH_2); contains about $\theta = 0.15$ molecules per surface Pt atom; is stable in vacuum and in solution over a wide range of electrode potentials; is replaced only slowly by other strong adsorbates such as iodide; and lacks long-range order in the absence of anions such as iodide. Related studies are exploring ionic adsorption, organic molecular adsorption, and electrodeposition of metallic monolayers.

G. Silicon Carbide Thin-Film Structure.

The structure of epitaxial β -SiC thin films grown on Si(100) has been investigated by measuring Auger electron emission angular distributions over an essentially complete hemisphere of angles of emission above the film surface (185). The β -SiC films were grown by rapid thermal chemical vapor deposition (RTCVD), in which the heated Si(100) surface was carbonized with propane. Auger emission angular distributions were measured for carbon at 268 eV, and for silicon at 86 eV and 1605 eV, allowing the thin film structure to be probed from the viewpoint of each element. The Auger measurements probe the thin film structure to a depth of several atomic layers. Each of the distributions displayed distinct, fourfold symmetric features, demonstrating the crystalline character of the β -SiC films. Comparison of the measured angular distributions with geometric projections and simulations for the known β -SiC structure indicates that the films consist of interspersed [100] crystalline domains (each domain having twofold symmetry),

with 90° in-plane rotational orientations between domains. These findings are consistent with STM observations of the outermost atomic layer. Crystalline SiC thin-films are important for Air Force electronic circuitry, having exceptional resistance to heat and ionizing radiation.

H. Implications of These Results

Voltammetric methods such as cyclic voltammetry, thin-layer electrochemistry and the closely related procedures of chronoamperometry, chronocoulometry, impedance measurements and other electrochemical (EC) techniques continue to be the most sensitive of the surface science methods applicable to smooth metal surfaces. There is presently no rival for the EC methods when used to "fingerprint" an adsorbate, to develop a quantitative calibration of the spectrum of a molecular or atomic layer, or to explore a charge-transfer process.

Auger spectroscopy has become an indispensable tool in connection with practical studies of metallic and semiconducting surfaces, including electrodes. Innovations which we have introduced recently have decreased the beam current requirements to about 10 nA/mm^2 , such that beam damage is seldom a factor. Surface cleanliness is verifiable by AES to within $\pm 1\%$ of an atomic layer in most cases. Surface elemental composition is quantifiable to within the accuracy of calibration, about $\pm 1\%$ relative. Surface layer stoichiometries (excepting hydrogen) are thus readily determinable. Packing densities (moles/cm^2) are accurately measurable by AES.

HREELS excels for detection of surface hydrocarbons and most other molecular species. Vibrational spectra are valuable clues to molecular identification at surfaces. Surface bonding and molecular constitution are readily explored by means of HREELS; resolution is moderate (60 cm^{-1}) while sensitivity is remarkable (about 0.001 monolayer in most cases). Frequency range spans both the far and near IR (60 cm^{-1} to 5000 cm^{-1} , routinely).

Surface IR is emerging as a versatile surface vibrational probe. Resolution is better than 4 cm^{-1} while sensitivity is beginning to rival that of HREELS with our instrumentation. The path to another ten-fold improvement in IR signal/noise ratio is straightforward during the next few months. IR has the advantages of applicability at ambient pressure and in the presence of electrolytic solutions, combined with complete molecular generality. As such IR is very sensitive to even the most subtle variations of surface molecular structure due to electrode potential, chemical conditions, or any other causes.

Angle-resolved Auger measurements are contributing to the fundamental understanding of the interaction of electrons with atoms, ions, molecules and solids,

and have longer-range potential applicability for probing surface structure at the level of atoms, molecules, and perhaps even chemical bonds.

Surface-sensitive spectroscopy combined with surface electrochemistry has powerful strengths for practical and fundamental characterization of solid surfaces. While IR, STM and other ambient-pressure techniques are very valuable, the electron diffraction and spectroscopic methods are also powerful, particularly for the vastly numerous and important systems in which chemisorbed layers are formed which are commonly found to be stable in vacuum. The connections among surface electrochemistry, surface characterization, and surface/thin-film materials processing in the electronics industry are very important for the future of clean manufacturing, cluster tool development, technological competitiveness, and flexible manufacturing, as illustrated by the MCT and SiC thin-film projects (168, 185).

II. PUBLICATIONS

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III SCIENTIFIC PERSONNEL

Arthur T. Hubbard. Principal Investigator. B.A., 1963, Westmont College; Ph.D., California Institute of Technology, 1967 (Graduate Adviser, Fred C. Anson). Professor of Chemistry, University of Hawaii, 1967-1976; Professor of Chemistry, University of California Santa Barbara, 1976-1986; Professor of Chemistry, Ohio Eminent Scholar and Director of the Surface Center, University of Cincinnati, 1986—present. Founding Associate Editor, *Langmuir*, the American Chemical Society's journal of surfaces and colloids, 1985-1990. Kendall Award for Surface or Colloid Chemistry, American Chemical Society, 1989; George Rieveschl, Jr., Award for Distinguished Scientific Research, University of Cincinnati, 1989; 41st Annual Cincinnati Chemist of the Year Award, American Chemical Society, Cincinnati Chapter, 1990; David C. Grahame Award of the Electrochemical Society, 1993. Please see refs. 16, 47, 111, 125, 167, in Section II, above.

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Arthur Case. Machinist. Ohio College of Applied Science, 1978-82. US Precision Lens, 1982-86.

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Richard Shaw. Technical Assistant. B.S., 1977, M.S., 1985, Bowling Green State University (Graduate Advisor, Vakula S. Srinivasan).

Hong Zhang. Graduate Student. B.S., 1982, M.S., 1985, Cheng Du University of Science and Technology.

IV. CURRENT AND PENDING SUPPORT**Current Support:****ARPA**

"Infrared Sensor Devices".

October, 1992 - September, 1993

\$100,000

October, 1993 - March, 1994

\$ 75,000

(10% of effort)

Pending Support:**AFOSR**

"Electrochemistry of Metal Surfaces".

May 1, 1993 - April 30, 1996

\$651,299

(10% of effort)